

Chapter 13

No handout

See powerpoint slides on wiki

**Chapter 14 Aqueous Equilibria:**

**Acids and Bases**

* **Bronsted Lowry theory:** an acid is a proton donor and a base is a proton acceptor (Worked Example 14.1 pg. 545
* A strong acid almost completely dissociates, a weak acid only partially dissociates. (Table 14.1 pg. 547
* Examples of strong acids: Examples of strong bases
  1. HClO4 1. H-
  2. HCl 2. O(2-)
  3. H2SO4 3. NH2-
  4. HNO3
* In the presence of an acid, water acts as a base and vice versa.
* **Kw=[H3O+][OH-]** characterizes the dissociation of water.
* **Kw=1x10^-14** (Worked Example 14.4 pg. 551)

If [H3O+] > [OH-] = Acidic

If [H3O+] = [OH-] = Neutral

If [H3O+] < [OH-] = Basic

* **pH= -log[H3O+]** pH< 7 =acidic

pH= 7=neutral **10^-pH = [H3O+]**

pH> 7=basic

* Strong acids and strong bases dissociate completely in water

(Worked Example 14.7 pg. 555)

* Ka is the equilibrium constant for an acid where:

Ka=concentrations of products = [H3O+][A-]

Concentrations of reactants [HA]

* + **pKa = -log Ka** (Worked Example 14.9 pg. 559)

**\*14.9 Review Powerpoint**

* Percent dissociation = [HA] dissociated x 100%

[HA] initial

\*concentration of acid that dissociates / initial acid concentration x 100

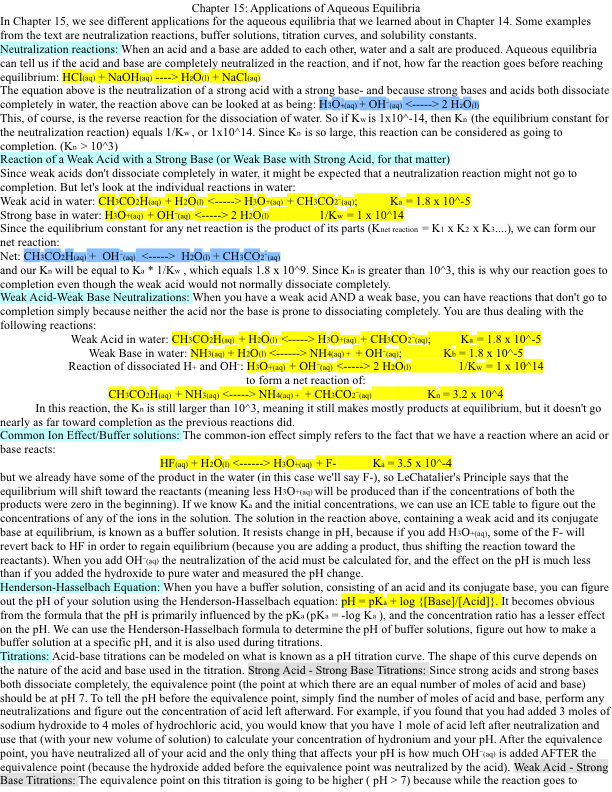
* Polyprotic acids have more than one proton that can dissociate
* This is denoted by Ka1 and Ka2 (Table 14.3)

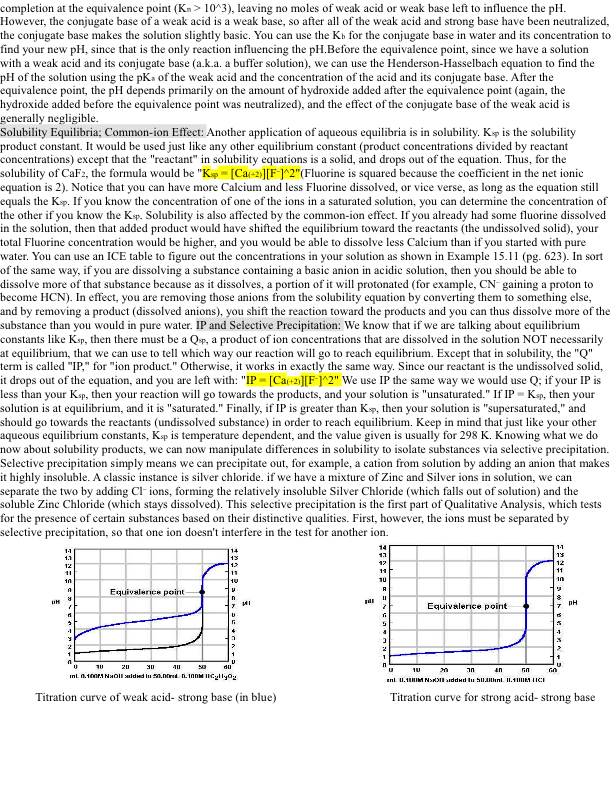
(Worked Example 14.11 pg. 566)

* Kb is the equilibrium constant for a base

Kb= concentrations of products = [BH+][OH-]

* + Concentrations of reactants [B]
* Ka x Kb = Kw pKa + pKb = 14
* A Lewis Acid is an electron pair acceptor and a Lewis base is an electron pair donor.
* Examples: Al(3+), Cu(2+), BF3, SO3, CO2





**Ch 16**

**Spontaneous Process:** as one that proceed on its own without any external influence. It always moves toward equilibrium.

Example: A stopcock is open; gas from bulb (a) expands to bulb b spontaneously until gas pressure in two bulbs are the same.

**Enthalpy**: Exchange of heat. Can be exothermic or endothermic.

**Entropy**: Molecular randomness. Whenever a molecule breaks into two or more pieces the molecular randomness increases.

Example: CO2 (s) ----> CO2 (g) – Randomness increases when a solid sublimes. Delta S Positive

2 N2 (g) + 3H2 (g) ----> 2NH3 (g) – Randomness is decrease. The number of gaseous molecules decrease from 4 moles to two moles. Meaning fewer molecules can move.

**Entropy and Temperature:** Temperature increases causes- Random molecular motion increase, broader distribution of individual molecular energies, more randomness and higher entropy.

**Standard Entropies** is measured in **Joules per Kelvin times moles**

**Delta S =** S (product) –S (reactant)

aA + bB ----> cC + dD

Delta S (system) = {c S(C) + d S (D) – a S (A) + b S (B)}

Delta S > 0 Reaction is spontaneous

Delta S < 0 Reaction is non spontaneous

Delta S = 0 Reaction is at equilibrium

Delta S total = Delta S system + Delta S surrounding

Delta S surrounding = - Delta H /Temperature

**Free Energy:**  Delta G = Delta H – T \* Delta S Or –T\*Delta S (total) = Delta G

-Temperature is the deciding factor that determines the importance of entropy and entropy contribution to delta G (free energy)

Refer to the chart below for different scenarios:

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Delta H | Delta S | Delta G= Delta H –T\*Delta S | Reaction Spontanity | Example |
| - | + | - | Spon at all temp | 2NO2(g)--->N2(g) + 2O2(g) |
| - | - | - or + | -Spon at low temp where delta H outweighs T\*Delta S  -non spon at high temps where T\*delta outweighs Delta H | N2(g) + 3H2(g)--->2NH3(g) |
| + | - | + | non spon at all temp | 3O2(g)--->2O3(g) |
| + | + | - or + | -spon at high temp where T\*Delta S outweighs Delta H  -nonspon at low temp where Delta H outweighs T\*delta S | 2HgO(s)--->2Hg(l) + O2(g) |

**Free energy changes and composition of the reaction mixture**: Delta G = Standard Delta G + RT ln Q

Example: Calculate free energy : N2(g) + 3H2(g) ----> 2NH3(g) standard delta G = -330. 0 kj. Given pressure in ATM

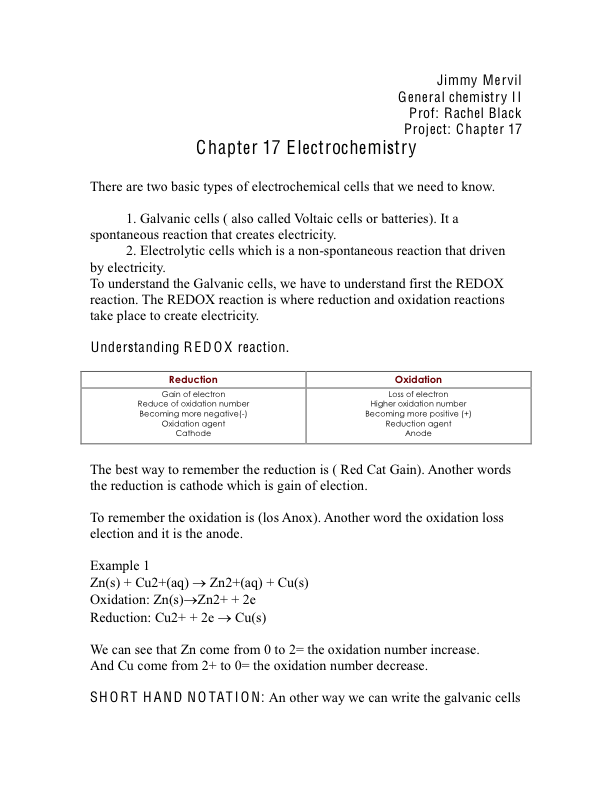
QP = P(NH3)2 / (PN2) (PH2)3

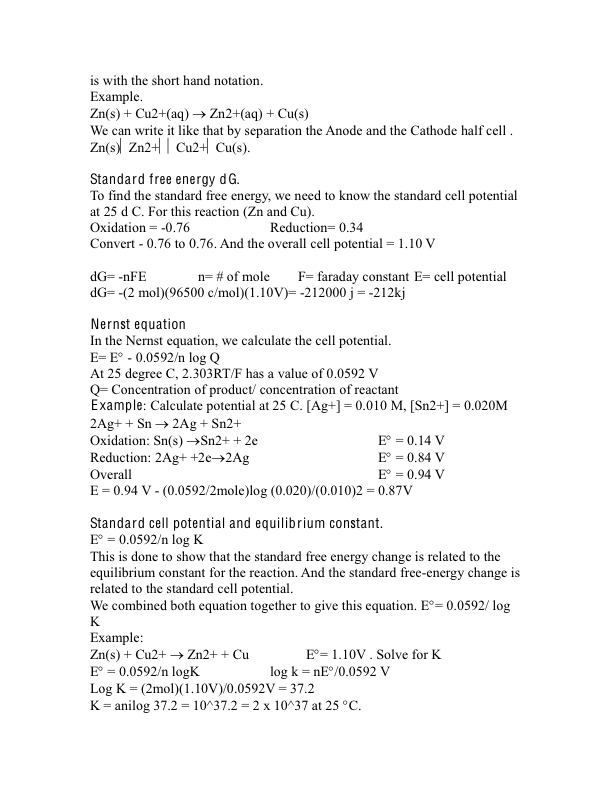
Delta G = -33000 j/mol + 8.314 j/k mol (298)(ln 1.5 \*10^-5)

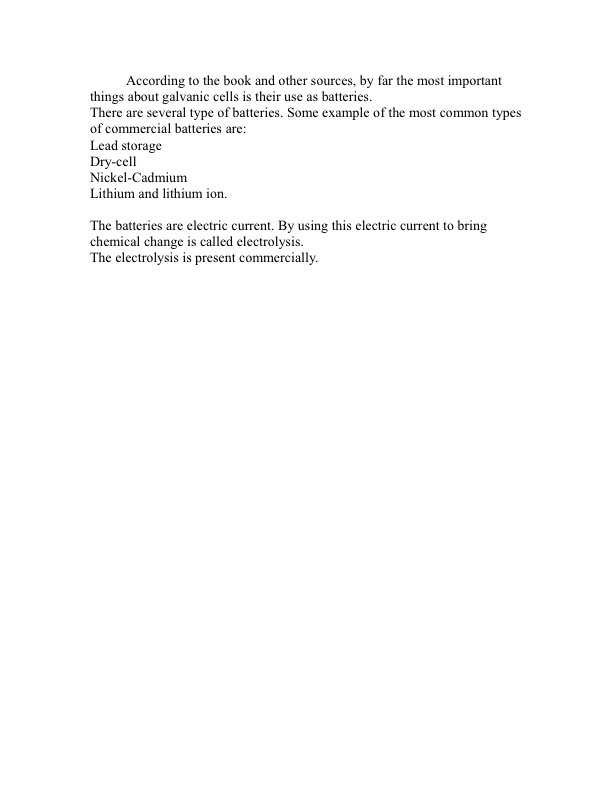
Delta G = -60.5kj/mol

**Relation ship between standard free energy change and equilibrium constant for a reaction**

|  |  |  |  |
| --- | --- | --- | --- |
| standard delta G | ln k | k | comment |
| SDG<0 | ln k > 0 | k>1 | equilibrium mainly products |
| SDG>0 | ln k < 0 | k<1 | equilibrium mainly reactants |
| SDG=0 | ln k = 0 | k=1 | equilibrium contains comparable amounts of reactants and products |







**Ch 18**

**Hydrogen Bonds** – intermolecular forces extremely weak; has very low melting point and low boiling point. Bonding forces between a H-H bond is extremely strong, bond dissociation is greater than any other single bond between two atoms of same element.

3 Isotopes of Hydrogen: Protium: ordinary hydrogen 1:1, deuterium or heavy hydrogen 2:1, and tritium 3:1. Properties of the three are all similar because of electronic structure however they have quantitative difference in properties (isotope effects) arises from the different masses of the isotopes. Isotopes effects are greater for hydrogen isotopes compared to other elements because of the percentage difference between masses.

**Hydrogen**: Reactivity: Because the amount of energy needed to ionize a hydrogen atom is very large hydrogen doesn’t completely transfer its valence electron in chemical reaction. Instead it shares this electron with a nonmetallic element to give a covalent compound. Examples Ch4, NH3. Complete ionization of hydrogen is possible in the gas phase. Hydrogen will accept an electron from a n active metal to give an ionic hydride. Example NaH or CaH2

Binary Hydrides: compounds that contain hydrogen and one other element. (ionic, covalent, or metallic)

**Ionic Hydrides**: salt like, high melting, white, crystalline compounds formed by alkali metals and heavier alkaline earth metals. Example: Ca, Sr, Ba. Example of a reaction is

2Na(l) + H2 (g) ----> 2NaH(s) Delta H = -112.6kj. Alkali metal hydrides contain alkali metal cation and H-anions

Covalent Hydrides: hydrogen attached to another element by a covalent bond. Example hydrides of nonmetallic elements (diborane) B2H6, ammonia NH3

Metallic Hydrides: formed by reaction of lanthanide and actinide metals and certain transitional metals with variable amount of hydrogen. General formula MHX ( X is subscript). Because hydrogen atoms can fill a variable number of interstices, many metallic hydrides are nonstoichiometric compounds-meaning that there atomic composition cant be express as a ration of small whole numbers.

Examples balance net ionic equations: Lithium hydride

LiH(s) + H2O(l)-----> H2(g) + Li(aq) + OH-(aq)

**Oxygen:** some information about oxygen: in all there phases –gas, liquid, solid O2 is paramagnetic. Bond length in O2 is 121 pm, which is shorter than O-O, bond dissociation energy of O2 is intermediate between that for the single bond F2 and triple bond N2. Oxygen is the most abundant element on the surface of our planet. Amount of oxygen in the atmosphere remain constant at 1.18 \* 10 ^18 kg

Reactivity: Can be anticipated by the electron configuration of oxygen atom (1s2 2s2 2p4)and its high electronegativity (3.5). Oxygen can achieve the octet configuration by accepting two electrons from a active metal or by gaining a share in two additional electron through covalent bonding. Example: 4Li (s) + O2---> 2Li2O(s) or covalent bond 2H2(g) + O2(g) ----> 2H2O(l) . Oxygen would rather from a double bond with a small atom such as carbon or nitrogen rather that a large atom such as silicon to overlap nicely.

Oxides: compounds with oxygen in the -2 oxidation state. Peroxides: compounds with oxygen in the -1 state. Superoxides: compounds with oxygen in the -1/2 state. Oxide can be categorized basic-an ionic that are formed by metals on the left side of the periodic table, acidic-are covalent and formed by nonmetals on the right side of the periodic metal, or amphoteric- which exhibit both basic and acidic type qualities.

Examples Basic: Na2O(s) +H2O(l)----> 2 Na(aq) + 2OH(aq)

Acidic: N2O5(s) + H2O(l) -----> 2H(aq) + 2NO3(aq)

Amphoteric: Basic Al2O3(s) + 6H(aq)---->2Al(aq) +3H2O(l)

Acidic AlO3 + 2OH-(aq) +3H2O---> 2Al(OH-)4- (aq)

Acidic character and covalent character of an oxide increases across the periodic table. Within a group both the basic character and the ionic character of a oxide increase going down the periodic table. Combining both trends you find that most acidic oxides are in the upper right of the periodic table. As the trends change so does the physical properties.

Finding oxidation number of Oxygen. Examples KO2 and SiO2

KO2: K is in group 1 A and has a oxidation number of +1, oxidation number of KO2 must be -1/2 (superoxide)

SiO2 Si is in group 4 A and has a oxidation number of +4, oxidation number of SiO2 must be -2 (oxide)

**Hydrogen Peroxide:** strong oxidizing agent and reducing agent. When acts as a oxidizing agent, oxygen from -1 oxidation state in H2O2 to the -2 oxidation state in H2O. When hydrogen peroxide acts as a reducing agent, oxygen is oxidized from -1 oxidation state in H2O2 to the 0 oxidation state in O2. H2O2 can oxidize and reduce itself, making it unstable and undergoes disproportionation to water and oxygen.

**Water**: essential to life. process to purify water include preliminary filtration, sedimentation-takes place in large tanks and is accelerated by the addition of lime and aluminum sulfate, sand filtration, aeration, and sterilization. (Hard Water) contains Ca 2+, Mg 2+, and Fe 2+. Can be soften by ion exchange in a process where Ca 2+ and Mg 2+ are replace with Na+

Reactivity: Water reacts with alkali metals and the heavier alkaline earth metals and halogens. Water is reduced to hydrogen by alkali and alkaline earth metals. Example

2Na(s) + 2H2O(l) ---> H2(g) + 2Na+ (aq) + 2 OH-(aq)

**Hydrates:** solid compound that contain water molecules. Examples: Magnesium percholorate hexahydrate Mg(ClO4)2 \* 6 H2O. Can determine the formula of a hydrate by knowing the grams of each hydrate obtained.

Ch 20-1 Electron Configurations

\*Key\*

Max amount of e- per orbital s =2, p =6, d =10, f =14

(Always start from the top right to the bottom left)

1s

2s 2p

3s 3p 3d

4s 4p 4d 4f

5s 5p 5d 5f

6s 6p 6d 6f

7s 7p 7d 7f

Ex. Ti: [Ar]3d0 4s2 there are 4 valence e-

\*\***The tricky ones**\*\*

Ex. Cr: [Ar]3d4 4s2 1 1 1 1 0 (3d) 2 (4s) prediction

1 1 1 1 1 (3d) 2 (4s) actual

Ex. Cu: [Ar]3d9 4s2 2 2 2 2 1 (3d) 2 (4s) prediction

2 2 2 2 2 (3d) 1 (4s) actual

\*\*\*\*\*In most cases the 4 shell ionizes easier than the 3 shell\*\*\*8

Ch 20-2 Properties

Ionization energies increase from left to right

The more to the right the harder it is to ionize

Ch 20-3 Oxidation States

Transition elements have a assortment of oxidation states

High oxidizing states are very easy to reduce

Ch 20-4 Chemistry of Transition

This section just talks about the commonly used transition elements that are used in the laboratory.

Chromium

Iron

Copper

Ch 20-5 Coordinate compounds

* One atom donates all of the electrons in a bond

Ligands – The molecules or ions that surround the central metal ion in a coordinate compound

Monodentate ligand – one attachment to a metal

Polydentate ligand – more than one attachment to a metal

Cis(together) Trans(opposite)

Cl- NH3

Cl- Pt+2 NH3 Cl- Pt+2 Cl-

NH3 NH3

Ch 20-7 Naming

\*\*Anything in the brackets is the coordination compound which is a discrete molecule.

1. Name all ligands
   1. If anionic ligand end in-o

ide-o

ate-ato

* 1. Use prefixes if have to (di, tri, tetra, etc….)

1. Name the metal
   1. Oxidation state in parenthesis

Ch 20-8 Isomers

* The atom is the same but with different properties

Constitutional isomers – physical connections are different. 2 types

1. Linkage
2. Ionization

Stereoisomer – same connection among atoms but a different arrangement of the atoms in space.

Diastereoisomers

Ch 20-9 Enantiomers

* Mirror images(nonsuper imposable)=chiral

Ch 20-10 Color

E2 excited state

E

E1 ground state (lowest energy level for a compound)